Static magnetic order in the triangular lattice of Li\(_x\)NiO\(_2\) (x ≤ 1): Muon-spin spectroscopy measurements

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In spite of numerous experimental and theoretical reports on LiNiO\(_2\), no consistent picture has emerged of the nature of its ground state. We have investigated the Li\(_x\)NiO\(_2\) system (0.1 ≤ x ≤ 1) by means of muon-spin spectroscopy and susceptibility to gain further insight from the effects of varying the magnetic ion concentration. Static magnetic order, most likely to be incommensurate to the spatial lattice period, was found for x ≥ 0.6 at low temperatures (T), while disordered magnetism due to localized Ni moments appears for x = 1/2 – 1/4 and, finally, Li\(_0.1\)NiO\(_2\) exhibits almost fully nonmagnetic behavior down to the lowest T measured. The ground state of LiNiO\(_2\) is inferred to be a “static but short-range” A-type antiferromagnetic ordered system, in which the Ni\(^{3+}\) moments align ferromagnetically along the c axis in the NiO\(_2\) plane with an incommensurate modulation probably due to canting of the Ni\(^{3+}\) moments, but align antiferromagnetically between adjacent NiO\(_2\) planes.

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I. INTRODUCTION

The two-dimensional triangular lattice (2DTL) antiferromagnet at half-filling has been investigated for an extended time both experimentally and theoretically because of the richness of its physics resulting from competition between the antiferromagnetic (AF) interaction and geometrical frustration. In the rhombohedral LiNiO\(_2\) lattice with space group \(R\bar{3}m\) (see Fig. 1), the NiO\(_2\) planes and Li layers form alternating stacks along the \(c_H\) axis in a hexagonal setting. In the NiO\(_2\) planes, Ni ions form a 2DTL by a network of edge-sharing NiO\(_6\) octahedra. Since the 2DTL planes are separated by nonmagnetic Li layers and Ni\(^{3+}\) is in the low spin state \((\frac{3}{2}, \frac{3}{2})\) with \(S=1/2\), LiNiO\(_2\) is thought to be an ideal material for elucidating frustrated magnetism on a half-filled 2DTL. Despite the half-filled state, LiNiO\(_2\) exhibits \(p\)-type semiconductivity in the whole temperature \(T\) range measured between 180 and 970 K.\(^1,2\) In early work, it was proposed that Ni\(^{3+}\) spins behave Ising-type with an easy axis along the \(c_H\) direction.\(^3\) Thus far, no long-range magnetic order has been detected down to the lowest \(T\) investigated.\(^3-6\) although the susceptibility shows a spin-glass-like (SG-like) anomaly around 10 K.\(^7\) Both heat capacity and NMR measurements, however, suggest a spin-liquid state with short-range ferromagnetic (FM) correlations.\(^5\) Positive muon-spin rotation and relaxation (\(\mu^+\)SR) experiments have also indicated the absence of static magnetic order down to 2 K as well as showing the existence of fast fluctuating moments.\(^5\) Recent neutron-diffraction (ND) experiments have also raised the possibility of local-orbital ordering of Ni\(^{3+}\) into three sublattices.\(^6\)

Past work revealed that the excess Ni is usually present in the Li layer of the LiNiO\(_2\) samples\(^7-9\) due to the similarity in ionic radii between Li\(^+\) and Ni\(^{3+}\). The ionic distribution of the Ni-excess LiNiO\(_2\) is thus given as \([\text{Li}^{+}][\text{Ni}^{2+}][\text{Ni}^{3+}][\text{O}_2]_6\), where Li ions occupy 3b, Ni ions 3a, and O ions 6c sites in the regular LiNiO\(_2\) lattice. The Ni\(^{2+}\) ions at the 3b site are known to introduce an additional interplane interaction, which alters the low-\(T\) magnetism from the spin-glass-like state below \(\sim 10\) K (\(< T_m\) for \(z=0\) to the ferro- or ferrimagnetic state at \(\sim 100\) K for \(z\) \(\geq 0.04\).\(^7,10\) In spite of efforts to prepare it, fully stoichiometric LiNiO\(_2\) (Refs. 10 and 11) is still unavailable and, as a result, the ground state of LiNiO\(_2\) continues to be under discussion.\(^12\)

The other layered nickel dioxides with a 2DTL such as rhombohedral NaNiO\(_2\),\(^13-15\) AgNiO\(_2\),\(^16-18\) and Ag\(_2\)NiO\(_2\) (Refs. 19 and 20) have also been investigated in order to clarify the ground state of the NiO\(_2\) plane. However, it is currently not possible to understand the nature of these compounds as a whole by a common physics framework.\(^21-25\) That is, NaNiO\(_2\) exhibits two transitions at \(T_{J} \sim 480\) K and \(T_N=20\) K. The former is a cooperative Jahn-Teller (JT) transition from a high-\(T\) rhombohedral phase to a low-\(T\) monoclinic phase, while the latter is a transition into an A-type AF phase, since ND and \(\mu^+\)SR experiments have shown ferromagnetic (FM) order in the NiO\(_2\) plane but AF order between

![FIG. 1. (Color online) Crystal structure of LiNiO\(_2\). (a) Alternating stacks along the \(c_H\) axis and (b) triangular lattice in the \(c_H\) plane.](image-url)
adjacent NiO$_2$ planes$^{13-15}$ In contrast, AgNiO$_2$ lacks a cooperative JT transition but has a long-range commensurate (C) AF ordered state with $T_N=21$ K caused by slight spatial deviation of the O$^{2-}$ ions, as was recently found by ND and $\mu$SR measurements.$^{17,18}$ For (Ag$_2$)$_x$Ni$_{1-x}$O$_2$, which also keeps a rhombohedral symmetry down to 2 K, static AF order, likely the formation of an incommensurate spin-density wave (IC-SDW) structure in the NiO$_2$ plane, was observed below $T_N=56$ K by a recent $\mu$SR experiment.$^{20}$

In order to further elucidate the nature of the NiO$_2$ plane and resolve the current confusing situation (see the introduction of Ref. 6, for example), we have chosen another approach to this subject, namely, to clarify the change in magnetism associated with changes of the valence of Ni ions, in other words, to know the variation of magnetism with the spin concentration on the 2DTL. For LiNiO$_2$, Li ions are easily deintercalated by electrochemical reaction down to $x \sim 0$ and, in fact, LiNiO$_2$ has been heavily investigated as a next generation cathode material of Li-ion batteries. The majority of previous research into Li$_x$NiO$_2$ has focused primarily on their structural and electrochemical properties with the aim of understanding their influence on the charge or discharge characteristics of Li-ion batteries. No systematic studies of the magnetic nature of Li$_x$NiO$_2$ at low $T$ have been carried out thus far, although $^7$Li-NMR results in the $T$ range above 263 K have recently become available.$^{28}$

In this paper, we describe our study of the microscopic magnetic nature of Li$_x$NiO$_2$ with $x=1, 3/4, 2/3, 3/5, 1/2, 1/3, 1/4,$ and 0.1 by means of $\mu$SR, which is very sensitive to the local magnetic and structural environments, because the implanted $\mu^+$’s response is dominated by the magnetic field generated by their nearest neighbors. We will discuss the $\mu$SR results in conjunction with bulk susceptibility measurements on the same samples. We demonstrate the existence of a variety of phases as a function of $x$ in Li$_x$NiO$_2$. In particular, the appearance of static magnetic order, most likely incommensurate (IC) order for Li$_x$NiO$_2$ with $x=1, 3/4, 2/3,$ and 3/5, suggests the A-type AF ordered state with an IC modulation in the plane for the ground state of the NiO$_2$ triangular lattice.

II. EXPERIMENTAL

A powder sample of LiNiO$_2$ was prepared at Osaka City University by a solid-state reaction technique using reagent grade LiOH$+\text{H}_2\text{O}$ and NiO powders as starting materials. A mixture of the two powders was heated at 750 °C for 12 h in an oxygen flow. Powder x-ray diffraction (XRD) analysis showed that the sample was single phase with a rhombohedral system of space group $R3m$ ($a_0=0.2875$ and $c_0=1.4191$ nm in a hexagonal setting). In order to estimate the excess Ni in the Li plane, $\chi$ was measured below 400 K under a $H=10$ kOe field with a superconducting quantum interference device (SQUID) magnetometer (MPMS, Quantum Design) for two powders (A and B) from another lot. Their Weiss temperature ($\Theta$) and effective magnetic moment ($\mu_{\text{eff}}$) were determined from $\chi(T)$ using a Curie-Weiss law in the range between 80 and 400 K to be 39–46 K and 2.04–2.08 $\mu_B$, respectively [see Figs. 2(a) and 2(b)]. In addi-

![](https://example.com/figure2.png)

**FIG. 2.** (Color online) $T$ dependences of the susceptibility ($\chi$) for two LiNiO$_2$ samples (A and B) from another lot. (a) and (b) The $\chi(T)$ and $1/\chi(T)$ curves obtained in FC mode with $H=10$ kOe and (c) the $\chi(T)$ curve obtained in both FC and zero-field cooling (ZFC) mode with $H=100$ Oe. Red lines in (a) and (b) represent a linear fit in the $T$ range between 80 and 400 K using a Curie-Weiss formula $\chi=C/(T-\Theta)$ and $C=(N\mu_B^2/3k_B)\mu_{\text{eff}}^2$. Here, $N$ is the number density of Ni spins, $g$ is the Landé $g$ factor, $\mu_B$ is the Bohr magneton, and $k_B$ is Boltzmann’s constant. We assumed $g=2$.

The Li-deficient samples were prepared by an electrochemical reaction using Li$|\text{LiPF}_6|$-ethylene carbonate-dimethyl carbonate$|\text{LiNiO}_2$ cells. The LiNiO$_2$ powder was pressed into a disk with 15 mm diameter and 0.4 mm thickness and the disk was used as a positive electrode. The Li$_x$NiO$_2$ disk was removed from the cell in a He-filled glove box just before the $\mu$SR measurement and then packed into a sealed powder cell. In order to assess possible changes in the Li-deficient samples during the $\mu$SR measurement, each sample was returned to the original cell afterwards to check their voltage (vs Li electrode). No significant change in the voltage, before and after the measurements, was observed. Their structures were subsequently confirmed by powder XRD and, finally, their compositions were checked by an induction-coupled plasma (ICP) analysis. The above procedure is essentially the same as that of our recent $\mu$SR work.
on Li$_3$CoO$_2$.\textsuperscript{30} The $\mu^+$SR experiments were performed on the $\pi$-E1 and $\pi$-M3 surface muon beam lines at PSI using an experimental setup and techniques described elsewhere.\textsuperscript{31}

III. RESULTS

A. Li$_x$NiO$_2$ with 3/5 $\leq x \leq 1$

Figures 3(a)–3(d) show the zero-field (ZF) $\mu^+$SR spectra at several temperatures for the four Li$_x$NiO$_2$ samples with $x \approx 3/5$ in the time domain up to 0.1 $\mu$s. Although the spectra for LiNiO$_2$ and Li$_{1.5}$NiO$_2$ exhibit only a first minimum around 0.025 and 0.04 $\mu$s, respectively, even at 1.6 K, the spectra for Li$_{3.4}$NiO$_2$ and Li$_{2.3}$NiO$_2$ clearly show two minima, unambiguously confirming a damped oscillation. The oscillation signal in a ZF spectrum, even if it is strongly damped, clearly signifies the appearance of static magnetic order in Li$_{3.4}$NiO$_2$ and Li$_{2.3}$NiO$_2$. We should note that, as $x$ decreases from 1, the second minimum clearly appears in the ZF spectrum for $x=3/4$ and $x=2/3$ at low $T$, but it has only the first minimum at $x=3/5$. This clearly demonstrates the effect of a competition between the magnetic interaction and spin concentration on static magnetic order. In other words, the ZF spectra for LiNiO$_2$ and Li$_{3.5}$NiO$_2$ should be explained by the same physics as those for Li$_{3.4}$NiO$_2$ and Li$_{2.3}$NiO$_2$.

Although the oscillating spectra can be fitted by a strongly damped cosine oscillation $\exp(-\lambda t) \times \cos(\omega_M t + \phi)$ due to static and C-AF order with wide field distribution, it is more reasonable to fit them by a zero-order Bessel function of the first kind $J_0(\omega_M t)$, which accounts for explaining the fast relaxing behavior in the early time domain (before 0.05 $\mu$s) and, more importantly, the extra 30$^\circ$–40$^\circ$ delay of the initial phase ($\phi$) required in the cosine fit for LiNiO$_2$ with $x=3/4$ and 2/3 (see Fig. 4). Here, the ZF spectrum described by $J_0$ is the well established signature that the $\mu^+$'s experience an IC magnetic field in the lattice,\textsuperscript{31} though there is a rare exception.\textsuperscript{32} More precisely, the ZF-$\mu^+$SR spectra at low $T$ were fitted with a combination of three signals

$$A_0 P_{\text{ZF}}(t) = A_{\text{IC}}\exp(-\lambda t) J_0(\omega_M t) + A_{\text{fast}}\exp(-\lambda_{\text{fast}} t) + A_{\text{slow}}\exp(-\lambda_{\text{slow}} t),$$

where $A_0$ is the maximum muon decay asymmetry, $A_{\text{IC}}$, $A_{\text{fast}}$, and $A_{\text{slow}}$ are the asymmetries of the $J_0$ signal due to static IC-AF order, a fast exponentially relaxation signal due to fluctuating moments which gives only minor contributions, and a slow exponentially relaxation signal due to the “1/3 tail” caused by the AF component parallel to the initial muon-spin polarization (plus an offset signal from the $\mu^+$’s stopped in the sample cell for LiNiO$_2$ with $x<1$), respectively. $\lambda_{\text{IC}}$, $\lambda_{\text{fast}}$, and $\lambda_{\text{slow}}$ are the relaxation rates of the corresponding signals.

While the ZF spectrum for the $x=3/4$ and 2/3 samples exhibits a clear damped oscillation at 1.6 K, the spectrum for the $x=1$ and 3/5 samples is so strongly damped that one can be sure only that the Ni moments freeze in a highly disordered fashion. We thus attempted to fit the ZF spectrum for LiNiO$_2$ using other possible functions, instead of $J_0$ in Eq. (1), namely, a damped cosine function, as in the case for the $x=3/4$ and 2/3 samples, and a dynamic Gaussian Kubo-Toyabe (KT) function $G_{\text{DGKT}}(t, \Delta, \nu)$ for a fluctuating disordered phase.

FIG. 3. (Color) Temperature dependence of zero-field $\mu^+$SR spectra for Li$_x$NiO$_2$ with $x=1$, 3/4, 2/3, and 3/5 [from (a) to (d)]. Solid lines represent the fit results using Eq. (1). Each spectrum is offset by 0.2 for clarity of display. The composition (Li/Ni ratio) determined by an ICP analysis is [from (a) to (d)] 0.97, 0.75, 0.65, and 0.61, respectively.

FIG. 4. (Color online) Fit results of the ZF-$\mu^+$SR spectrum for (a) and (b) Li$_{3.4}$NiO$_2$ and (c) and (d) Li$_{2.3}$NiO$_2$ at 1.6 K. The fit using a Bessel function ($J_0$) for an incommensurate order [(a) and (c)] provides a reasonable result, while the fit using a cosine oscillation [(b) and (d)] gives almost the same result as that of the Bessel function, but the obtained delay of the initial phase ($\phi \approx -30^\circ$–$-40^\circ$) is physically meaningless. Since the fit was performed to minimize $\chi^2$, reduced $\chi^2 (=\chi^2/N)$ is shown for comparison, where $N$ is degree of freedom. There are eight parameters in Eq. (2), whereas seven parameters in Eq. (1). The cosine fit thus yields slightly better reduced $\chi^2$ than the Bessel fit.
FIG. 5. (Color) Fit results of the ZF-μSR spectrum for (left) LiNiO$_2$ (B) and (right) Li$_{3.5}$NiO$_2$ at 1.6 K. Note that a Kubo-Toyabe function for a random disordered phase needs an additional fast relaxing component [exp(-λ$_{fast}$t)] with almost the same amplitude to that of the KT component (see Table I).

$$A_0P_{ZF}(t) = A_{AF}e^{-\lambda_{AF}t} \cos(\omega_{AF}t + \phi) + A_{fast}e^{-\lambda_{fast}t} + A_{slow}e^{-\lambda_{slow}t},$$

(2)

$$A_0P_{ZF}(t) = A_{KT}G^{DGKT}(t, \Delta, \nu) + A_{fast}e^{-\lambda_{fast}t} + A_{slow}e^{-\lambda_{slow}t},$$

(3)

where $A_{AF}$ and $A_{KT}$ are the asymmetries of the C-AF and KT signals, $\lambda_{AF}$ is the relaxation rates, $\omega_{AF}$ is the muon Larmor frequency for the C-AF ordered field, $\phi$ is the initial phase of the precession, $\Delta$ is the static width of the local frequencies at the disordered sites, and $\nu$ is the field fluctuation rate. When $\nu=0$, $G^{DGKT}(t, \Delta, \nu)$ is a static Gaussian Kubo-Toyabe function $G^{KT}(t, \Delta)$ given by

$$G^{KT}(t, \Delta) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2/2) e^{-\Delta^2/2}. \tag{4}$$

The fit results using Eqs. (1)–(3) are shown in Fig. 5 and the obtained parameters are listed in Table I. The KT fit yields that $\Delta = 76.88(1) \times 10^6$ s$^{-1}$ and $\nu = 0.18(5) \times 10^6$ s$^{-1}$ for LiNiO$_2$ [$\Delta = 49.73(3) \times 10^6$ s$^{-1}$ and $\nu = 0.17(4) \times 10^6$ s$^{-1}$ for Li$_{3.5}$NiO$_2$], indicating the static nature of the disordered field because $\Delta \gg \nu$. This is inconsistent with the past high-longitudinal field $\mu^+\text{SR}$ result. Moreover, the fact that $A_{fast}/A_{KT} \sim 0.8$ for LiNiO$_2$ (0.7 for Li$_{3.5}$NiO$_2$) in turn provides two possibilities: one is that there are two magnetically inequivalent muon sites in the lattice and the other is coexistence of two different magnetic phases in the sample at low $T$. If there are two inequivalent muon sites in the LiNiO$_2$ lattice, the magnetic environment responsible for the KT signal is static, whereas that for the $A_{fast}$ signal is dynamic. Such a situation is very unlikely to be applicable for the LiNiO$_2$ lattice because of the short distance between the two adjacent NiO$_2$ planes. Furthermore, electrostatic potential calculations suggest that muons locate at the vicinity of $O^-$ ions, as in the case for LiCoO$_2$ (Ref. 30) and NaNiO$_2$. This also excludes the possibility that the two magnetically different muon sites coexist in the LiNiO$_2$ lattice. On the other hand, concerning the possibility of an intrinsic phase separation at low $T$, there are no evidences in past NMR measurements. In addition, the ratio $A_{fast}/A_{KT}$ for LiNiO$_2$ is comparable to that for Li$_{3.5}$NiO$_2$, although the ratio would be expected to depend on $x$, if we assume the reaction $\text{LiNiO}_2 \rightarrow y\text{Li}_1\text{NiO}_2 + (1-y)\text{Li}_2\text{Ni}_2\text{O}_5$ ($x \gg x \gg x$) for both samples. As a result, the KT fit is most unlikely to explain the magnetic nature of LiNiO$_2$ and Li$_{3.5}$NiO$_2$. The cosine

<table>
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<th>Equation</th>
<th>$A_{main}$</th>
<th>$A_{fast}$</th>
<th>$\lambda_{fast}$ ($10^6$ s$^{-1}$)</th>
<th>$A_{slow}$</th>
<th>$\lambda_{slow}$ ($10^6$ s$^{-1}$)</th>
<th>$\chi^2/N$</th>
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<tr>
<td>LiNiO$_2$, $A$</td>
<td>(1) $J_0$</td>
<td>0.1690(8)</td>
<td>0.03480(2)</td>
<td>9.66(11)</td>
<td>0.0362(8)</td>
<td>0.507(2)</td>
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<td></td>
<td>(2) $\cos$</td>
<td>0.166(2)</td>
<td>0.038(2)</td>
<td>11.0(1.3)</td>
<td>0.036(4)</td>
<td>0.52(4)</td>
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<tr>
<td></td>
<td>(3) $G^{DGKT}$</td>
<td>0.1018(2)</td>
<td>0.1157(2)</td>
<td>56.0(1.8)</td>
<td>0.0225(4)</td>
<td>4.5(3)</td>
</tr>
<tr>
<td>LiNiO$_2$, $B$</td>
<td>(1) $J_0$</td>
<td>0.175(4)</td>
<td>0.037(2)</td>
<td>6.1(8)</td>
<td>0.028(6)</td>
<td>0.25(7)</td>
</tr>
<tr>
<td></td>
<td>(2) $\cos$</td>
<td>0.175(4)</td>
<td>0.037(3)</td>
<td>6.0(8)</td>
<td>0.033(3)</td>
<td>0.28(7)</td>
</tr>
<tr>
<td></td>
<td>(3) $G^{DGKT}$</td>
<td>0.116(2)</td>
<td>0.092(10)</td>
<td>53(4)</td>
<td>0.03(1)</td>
<td>4.1(2)</td>
</tr>
<tr>
<td>Li$_{3.5}$NiO$_2$</td>
<td>(1) $J_0$</td>
<td>0.158(3)</td>
<td>0.028(4)</td>
<td>7.9(1.4)</td>
<td>0.054(1)</td>
<td>0.34(3)</td>
</tr>
<tr>
<td></td>
<td>(2) $\cos$</td>
<td>0.156(3)</td>
<td>0.030(3)</td>
<td>8.7(1.2)</td>
<td>0.033(3)</td>
<td>0.35(3)</td>
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<tr>
<td></td>
<td>(3) $G^{DGKT}$</td>
<td>0.116(5)</td>
<td>0.082(4)</td>
<td>22(2)</td>
<td>0.03(1)</td>
<td>0.71(9)</td>
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oscillation model provides almost the same goodness of fit as the Bessel function, but the obtained delay of the initial phase ($\phi \sim -40$ to $-60^\circ$) is physically meaningless. This indicates that the cosine fit is unsuitable in this case.

Although it is very hard to infer whether the traces of order reflect IC-, C-AF tendencies, or a Kubo-Toyabe behavior for LiNiO$_2$ based only on the present results, the fits to a critically damped IC-AF give an overall more reasonable explanation for the magnetism of LiNiO$_2$. Unfortunately, $\mu^*$SR provides no information on the correlation length of static magnetic order. However, since both NMR and neutron measurements showed an absence of long-range order for LiNiO$_2$, the static order detected by $\mu^*$SR is likely to be “short-ranged” from the NMR and/or neutron-diffraction viewpoint.

Figure 6 shows the $T$ dependences of the $\mu^*$SR parameters for the two LiNiO$_2$ samples (A and B of Fig. 2) and the Li$_4$NiO$_2$ samples with $x=3/4$, 2/3, and 3/5 obtained from the ZF and weak transverse field (wTF) data with wTF=30 Oe. Since the normalized wTF asymmetry ($N_{A_{TF}}$) is roughly proportional to the volume fraction of paramagnetic phases, it is found that the whole sample enters into the magnetic phase below $\sim 16$ K ($=T_{\text{mid}}$, at which $N_{A_{TF}}=0.5$) for LiNiO$_2$, $\sim 37$ K for Li$_{3/4}$NiO$_2$, $\sim 32$ K for Li$_{2/3}$NiO$_2$, and $\sim 10.5$ K for Li$_{3/5}$NiO$_2$. As $T$ decreases from $T_{\text{mid}}$, $f_{IC}$ increases with decreasing slope ($df_{IC}/dT$) and finally reaches around 22 MHz for LiNiO$_2$, $\sim 33$ MHz for Li$_{3/4}$NiO$_2$, $\sim 30$ MHz for Li$_{2/3}$NiO$_2$, and $\sim 14$ MHz for Li$_{3/5}$NiO$_2$ at the lowest $T$ measured, as expected for the order parameter of the IC-AF (IC-SDW) state. Considering the “1/3 tail” component due to the powder average, the normalized $A_{IC}$ suggests that almost the whole sample is in the IC-AF state below $\sim 10$ K for LiNiO$_2$, $\sim 30$ K for Li$_{3/4}$NiO$_2$, $\sim 25$ K for Li$_{2/3}$NiO$_2$, and $\sim 5$ K for Li$_{3/5}$NiO$_2$.

Although $T_{\text{mid}}=10$ K was determined by $\chi$ measurements with $H=10$ Oe [11 K with $H=100$ Oe, see Fig. 6(d)], the present $\mu^*$SR data yield that $T_{\text{mid}}=16$ K with static order appearing below 12 K for the almost stoichiometric LiNiO$_2$. 
Due to the wide distribution of the internal field observed, which results in a large $\lambda_{SC}$ even at 1.6 K, it would be very difficult to detect static order by other techniques. In the previous $\mu^+\text{SR}$ experiment on Li$_2$NiO$_2$, the early time domain and the low $T$ regime were not explored in enough detail to detect the ordering below 10 K.\textsuperscript{5}

### B. Li$_x$NiO$_2$ with $x \leq 3/5$

The ZF spectra for Li$_{1/2}$NiO$_2$, Li$_{1/3}$NiO$_2$, and Li$_{1/4}$NiO$_2$ exhibit a simple relaxation due to fluctuating moments, but the relaxation rate of Li$_{1/2}$NiO$_2$ is smaller than those of Li$_{1/3}$NiO$_2$ and Li$_{1/4}$NiO$_2$ [see Fig. 7(b)], suggesting a possible Li$^+$ ordering and/or charge ordering similar to the case of Na$_0.3$CoO$_2$.\textsuperscript{34-36} The ZF spectrum for Li$_{1/3}$NiO$_2$ is almost time independent, which is consistent with the fact that, as $x$ decreases from 1, the magnetic Ni$^{3+}$ ions are converted to nonmagnetic Ni$^{4+}$ ions ($I_{2/3}, S=0$) (Ref. 37) to finally reach Li$0$Ni$^{4+}$O$_2$. As seen in Fig. 7(a), the wTF measurements suggest a bulk magnetic transition with $T_N^{\text{mid}}=4$ K for $x=1/2$, 6 K for $x=1/3$, and 6.5 K for $x=1/4$. This indicates that these three samples exhibit a transition from the high-$T$ paramagnetic to the low-$T$ static disordered phase, i.e., a spin-glass-like phase at $T_N$, as in the case for the related compounds with the CoO$_2$ plane.\textsuperscript{38}

### C. Comparison with $\chi$

For the Li$_x$NiO$_2$ samples with $x < 1$, all the $\chi(T)$ curves exhibit a clear cusp around 10 K ($=T_m$) regardless of the value of $x$, different from $T_N$ determined by $\mu^+\text{SR}$ (see Fig. 8). This means that $T_m$ is induced by a minor component (below a few percent) in the sample, probably due to a very small amount of Ni ions at the 3b site. We wish therefore to emphasize that, since the cusp does not reflect the bulk magnetism, it is very hard or, in some case, may even be misleading to investigate the magnetic nature of Li$_x$NiO$_2$ only by $\chi$ measurements. In other words, $\mu^+\text{SR}$ is the most suitable technique for such purpose.

Figure 9 shows the $T$ dependence of $\chi$ for Li$_x$NiO$_2$ measured in field-cooling (FC) mode with $H=10$ kOe in order to study its macroscopic magnetic nature as a function of $x$. Roughly speaking, the $\chi(T)$ curve for the samples with $x>0.5$ exhibits a linear $T$ dependence above 100 K, while that for the $x\leq1/2$ samples shows a nonlinear, i.e., a convex-type $T$ dependence. A Curie-Weiss fit in the $T$ range between 200 and 350 K yields a positive $\Theta$ for all $x$ range down to 1/10, although $\mu_{\text{eff}}$ decreases monotonically with decreasing $x$ as expected [see Figs. 9(b) and 9(c)]. Interestingly, as $x$ decreases from 1, $\Theta$ increases from $\sim$40 to $\sim$55 K at around $x=0.8$ and then $\Theta$ decreases down to $\sim$15 K at $x=0.5$. Below $x=0.5$, $\Theta$ seems to increase again with decreasing $x$, although it is difficult to estimate it precisely from the convex-shaped $\chi(T)$ curve. In other words, the $\Theta(x)$ curve exhibits a broad maximum at $x=0.8$, around which $\mu^+\text{SR}$ detects a clear oscillation at low $T$. Actually, there is a good correlation between $\Theta$ and $T_N$ ($T_m$) determined by $\mu^+\text{SR}$, as seen in Fig. 9(b). This means that the static magnetic order is induced mainly by a FM interaction, although the spontaneous magnetization has not been observed at low $T$ for all the samples.

### IV. DISCUSSION

Since the Li-deficient samples are unstable in air and it is hard to prepare a proper amount for ND measurements...
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FIG. 9. (Color) (a) Temperature dependence of $\chi^{-1}$ for Li$_x$NiO$_2$ with 0.1 $\leq x \leq$ 1 measured in FC mode with $H=10$ kOe, the relationship between (b) Weiss temperature ($\Theta$) and $x$ and (c) the effective magnetic moment ($\mu_{\text{eff}}$) and $\theta$ with $H=10$ kOe, were obtained by fitting the $\chi^{-1}(T)$ curve in the $T$ range between 200 and 350 K using a Curie-Weiss formula $\chi=\chi_0+\Theta/(T-\Theta)$. Here, $\chi_0$ is a $T$-independent $\chi$ in order to fit the convex-shape $\chi^{-1}(T)$ curve. In (b), $T_N$ and $T_t$ determined by the $\chi$-type $\mu$SR measurements are also plotted for comparison.

(10 cm$^3$), information on their magnetic structure is currently unavailable. Here, we discuss their magnetic structure in relation to the present $\mu$SR and $\chi$ results using two possible structures, namely, A-type AF order with an IC modulation in the NiO$_2$ plane or, alternatively, IC-SDW order in the NiO$_2$ plane.

According to the above $\chi$ measurements, the predominant interaction between the Ni moments is most likely FM. This would directly lead to FM order of the Ni moments in the NiO$_2$ plane. The absence of bulk ferromagnetism suggests that the FM-ordered plane is coupled antiferromagnetically, i.e., A-type AF order as for NaNiO$_2$. Past magnetizations and ND measurements on NaNiO$_2$ have shown that the in-plane FM coupling constant ($J_{\text{FM}}$) is 29 K and the interplane AF coupling constant ($J_{\text{AF}}$) is $-1.9$ K. 8,14,13,39 but with $\Theta=35$ K and $T_N=20$ K. Since this $\Theta$ is comparable to those for Li$_x$NiO$_2$ with $x \geq 3/5$ [see Fig. 9(b)], it is reasonable to assume the similar values of $J_{\text{FM}}$ and $J_{\text{AF}}$ for Li$_x$NiO$_2$, resulting in A-type AF order at low $T$. This is also consistent with the fact that both the $T_2(x)$ and $\Theta(x)$ curves show their maximum at around $x=0.8$.

In order to explain the IC nature detected by $\mu$SR, we need to introduce an IC modulation of the ordered moments in the plane because such modulation is very unlikely to appear along the $c_{\parallel}$ axis. Here, we should note that the direction of the ordered moment ($\mu_{\text{ord}}=0.97$ $\mu_B$) for NaNiO$_2$ is canted by $\sim 10^\circ$ from the $c_{\parallel}$ direction. 13 The in-plane component ($0.18$ $\mu_B$) also aligns ferromagnetically along the $a_{\parallel}$ axis in the plane, but antiferromagnetically between the neighboring planes. 13 Assuming that $\mu_{\text{ord}}$ is also canted for LiNiO$_2$, FM order of the in-plane component would be strongly perturbed by the Ni ions in the Li layer because such Ni ions induce an additional interplane interaction through the Ni$_2$O$_7^{2-}$-Ni$_3^{3+}$-Ni$_{3a}$ coupling in [Li$_{1-x}$Ni$_{2+}$]$^{3+}$[Ni$_{3a}^{3+}$Ni$_{3c}^{2+}$]$_{2x}$O$_6$]. As a result, although the Ni moments mainly align along the $c_{\parallel}$ axis, the in-plane component would form a spin-pattern, which was predicted for the vortex-lattice state on the 2DTL, 40 around the Ni$_{3a}$ ions located just below or above the Ni$_{3c}^{3+}$ ions in the Li layer. Furthermore, since the Ni$_{3c}^{2+}$ ions distribute randomly in the Li layer so as to minimize electrostatic repulsion, the obtained spin-pattern would be expected to be incommensurate to the 2DTL.

For NaNiO$_2$, although $\mu_{\text{eff}}=1.85$ $\mu_B$, $\mu$SR measurements showed that $f_{\text{AF}}(0 K) \sim 64$ MHz. 15 This value is two or three times higher than those for Li$_x$NiO$_2$, while $\mu_{\text{eff}}$ is comparable to that for LiNiO$_2$ ($\sim 2.0$ $\mu_B$). This means that either $\mu_{\text{ord}}$ for LiNiO$_2$ is smaller than that for NaNiO$_2$ (0.97 $\mu_B$) or that the angle between $\mu_{\text{ord}}$ and $c_{\parallel}$ plane for LiNiO$_2$ is smaller than that for NaNiO$_2$ ($\sim 10^\circ$). Since the distance between the two adjacent NiO$_2$ planes is 0.473 nm for LiNiO$_2$ and 0.52 nm for NaNiO$_2$, 14 the canting angle of $\mu_{\text{ord}}$ for LiNiO$_2$ is naturally expected to be larger than that for NaNiO$_2$, resulting in a larger in-plane component of $\mu_{\text{ord}}$. Therefore, IC order of the in-plane component would decrease the internal magnetic field, as observed by the present $\mu$SR data.

If the intraplane coupling is AF, theoretical studies based on the Hubbard model have predicted the appearance of IC-SDW order on the 2DTL. 42,43 and $U/t$ and the spin concentration ($n$), where $U$ is the on-site repulsion and $t$ is the electron transfer. When $n=1/2$, as $U/t$ increases from 0, a paramagnetic phase changes to an IC-SDW phase at $U/t=3.97$ and then to a classical 120° AF phase at $U/t=5.27$. We could then deduce that 3.97 $\leq U/t \leq$ 5.27 for LiNiO$_2$, although the local-orbital ordering hinders the formation of long-range order detectable by ND and/or NMR measurements. 8 The decrease in $n$ from 1/2 is thought to suppress geometrical frustration, resulting in further stabilization of the IC-SDW phase for Li$_x$NiO$_2$ with $x=3/4$. The decrease in $T_N$ and $f_{\text{fc}}$ (and increase in $\lambda_{\text{fc}}$) with further lowering $x$ could be explained by the decrease in the spin concentration, i.e., the number density of the nearest neighboring Ni moments. This could be, therefore, a reasonable explanation for the change in magnetic nature of Li$_x$NiO$_2$ with decreasing $x$ from 1 to 3/5, although a theoretical treatment to describe the magnetic phases formed on the 2DTL as a function of $n$ and $U/t$ is not currently available.
FIG. 10. (Color) (a) Schematic phase diagram of Li$_x$NiO$_2$ determined by $\mu^+\text{SR}$ and the $x$ dependences of (b) $T_m$, which corresponds to the cusp $T$ in the $\chi(T)$ curve measured in ZFC mode with $H=100$ Oe. Here, $T_N$ and $T_f$ are the $T$ at which $N_{\text{eff}}(T)=0.5$. In (a), AF stands for an incommensurate antiferromagnetic ordered phase and SG a spin-glass-like phase. The phase boundary between AF and SG phases is still ambiguous at present.

Considering the overall results, including past work, we conclude that $A$-type AF order with an in-plane IC modulation is a reasonable description of the ground state for Li$_x$NiO$_2$. The Ni ions in the Li layer, however, naturally hinder the formation of long-range order, which would be detectable by ND and/or NMR whether the additional interplane interaction is FM or AF. On the other hand, since muons mainly sense the local magnetic field generated by the nearest neighboring moments, $\mu^+\text{SR}$ has provided information on static but short-range magnetic order for Li$_x$NiO$_2$ with 3/5 $\leq x \leq 1$. This conclusion is, therefore, consistent with the ground state for LiNiO$_2$ proposed by NMR, i.e., a spin-liquid state with short-range FM correlations.

Finally, we present a schematic magnetic phase diagram for Li$_x$NiO$_2$ based on the present $\mu^+\text{SR}$ results (see Fig. 10). A dome-shaped AF phase region exists in the $x$ range between $\sim 0.55$ and 1, whereas the SG-like phase appears below $x \sim 0.55$, and the paramagnetic phase is stable below $x=0.1$, down to the lowest $T$ measured. The dome-shaped boundary of the AF phase indicates the competition between the spin concentration and the FM interaction on the 2DTL of the NiO$_2$ plane.

V. SUMMARY

Thanks to the unique power of $\mu^+\text{SR}$, we have found the formation of static magnetic order, i.e., $A$-type AF order with an in-plane IC modulation, for Li$_x$NiO$_2$ with $x=3/4$ and 2/3 below around 35 K, while the $\chi(T)$ curve exhibits no anomalies in the same $T$ range. The careful analysis of the ZF spectrum for LiNiO$_2$ and Li$_{1.5}$NiO$_2$ reveals that their ground states are also most likely an $A$-type AF ordered phase, but short ranged. On the other hand, Li$_x$NiO$_2$ with $x \leq 1/2$ is found to enter into a spin-glass-like phase at low $T$, but Li$_{1.5}$NiO$_2$ is paramagnetic down to the lowest $T$ measured. These results are explained by competition between the concentration of FM coupled spins and $J_{\text{FM}}$ on the NiO$_2$ triangular lattice.

Our systematic $\mu^+\text{SR}$ study on Li-battery materials has clarified their interesting microscopic magnetic and structural natures, which are very sensitive to the Li content. This is because such materials include a rigid lattice as a skeleton, which provides open paths for mobile Li$^+$ ions. Since the skeleton is usually formed by a two-dimensional triangular lattice, Kagome-lattice, or spinel (pyrophylite) lattice of transition metals, the combination of electrochemical Li-deintercalation techniques with $\mu^+\text{SR}$ is a powerful method to detect the change in magnetic nature of these frustrated systems as a function of the spin concentration, as illustrated by the present results in Fig. 10.

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